

## Preparation and Characterization of Graphite Anodes For Lithium Ion Batteries

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The lithium-ion batteries are energy storage systems of high performance and low cost. They are employed in multiple portable devices and these require the use of increasingly smaller and lighter batteries with high energy and power density, fast charging and long service life. Moreover, these systems are promising for use in electric or hybrid vehicles. However, the lithium-ion battery still requires to improve the electrode materials properties, such as cost, energy density, cycle life, safety, and environmental compatibility. These batteries use carbon as anode material, usually synthetic graphite, because of its high coulombic efficiency and acceptable specific capacity for the formation of intercalation compounds (LiC<sub>6</sub>). In this paper the methodology used to prepare and characterize the reversible and irreversible capacity and, cyclic stability of graphite materials as anodes in lithium-ion batteries of commercial carbon and Sungite carbon, is presented. The results obtained using electrochemical techniques, are discussed.

### Introduction

The escalating demand for high-energy-density Li-ion batteries has led to increasing focus on finding alternatives to existing graphite anode materials, with higher storage capacities. Si-based anodes has emerged as a viable candidate due to its high theoretical specific capacity (Li<sub>4.4</sub>Si: 4200 mAhg<sup>-1</sup>). However, lithiation and delithiation processes result in a drastic volume change with consequent mechanical disintegration of the electrode, and rapid capacity fading in the subsequent cycles. The expended efforts to improve the electrochemical performance of anodes, as discussed in detail in recently published papers (1-16).

Artificial graphite has been considered a very good high powered anode material in the Lithium-ion batteries, even with better electrochemical performance than natural graphite (17-19). Graphite has been widely used in different commercial applications because of their good properties, such as: stability of the electrode/electrolyte interphase, the low and flat operating voltage and the relatively high specific capacity (20). Recently, many different types of artificial graphite materials (cokes, carbon fibers, mesocarbon microbeads (MCMBs), anthracite, etc. have been studied as anodes for high power lithium-ion batteries (21).

In this work the preparation and characterization, using optic and electrochemical techniques, of graphite materials (commercial carbon and Sungite carbon) as anodes for lithium-ion batteries are presented. The structure and chemical composition of the materials were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM). The electrochemical characterization was carried out using charge-discharge curves at different current densities, cyclic voltammetry and electrochemical impedance spectroscopy (EIS) techniques.

## **Experimental**

Scanning electron microscopy (SEM, FEI Quanta 650 FEG) along with the X ray Energy Dispersive Spectroscopy (EDX) analysis were used to study the surface properties and chemical composition respectively. Transmission electron microscope (TEM) micrographs were acquired with a FEI Tecnai G2 F20.

Electrochemical cells were assembled with sungite and commercial carbon as working electrodes, lithium foil as counter electrode, and LiPF<sub>6</sub> 1M in ethylene carbonate: dimethyl carbonate (EC:DMC) 1:1 w/w was used as electrolyte. All electrochemical tests were performed at room temperature. The cells were galvanostatically cycled, at 0.5C, in the potential range 0.0 to 1.5V and 0.0 to 2.5 V vs. Li/Li for commercial carbon and sungite electrodes respectively, using a VMP3 multi-channel galvanostat-potentiostat-EIS (Bio-Logic).

EIS measurements were performed using a superimposed AC voltage amplitude of 5 mV in the frequency range of 0.1 to 100.000 Hz. Then, the rate capability performance of the cells was studied at different C-rates (0.25C, 0.5C, 1C, 2C, 5C and 10C) during 4 cycles.

## **Results and discussion**

### **Characterization of samples**

Figure 1 shows SEM images (10000X) and the corresponding EDS analysis of sungite (Fig. 1 (a)) and commercial carbon samples (Fig. 1 (b)). Sungite samples exhibit morphology of plate shape type, however the commercial carbon materials present a kind of thin sheet plates structures. The EDS spectrum of the materials shows composition. For sungite, the EDS analysis shows that transition metals are present in the sungite of sample.

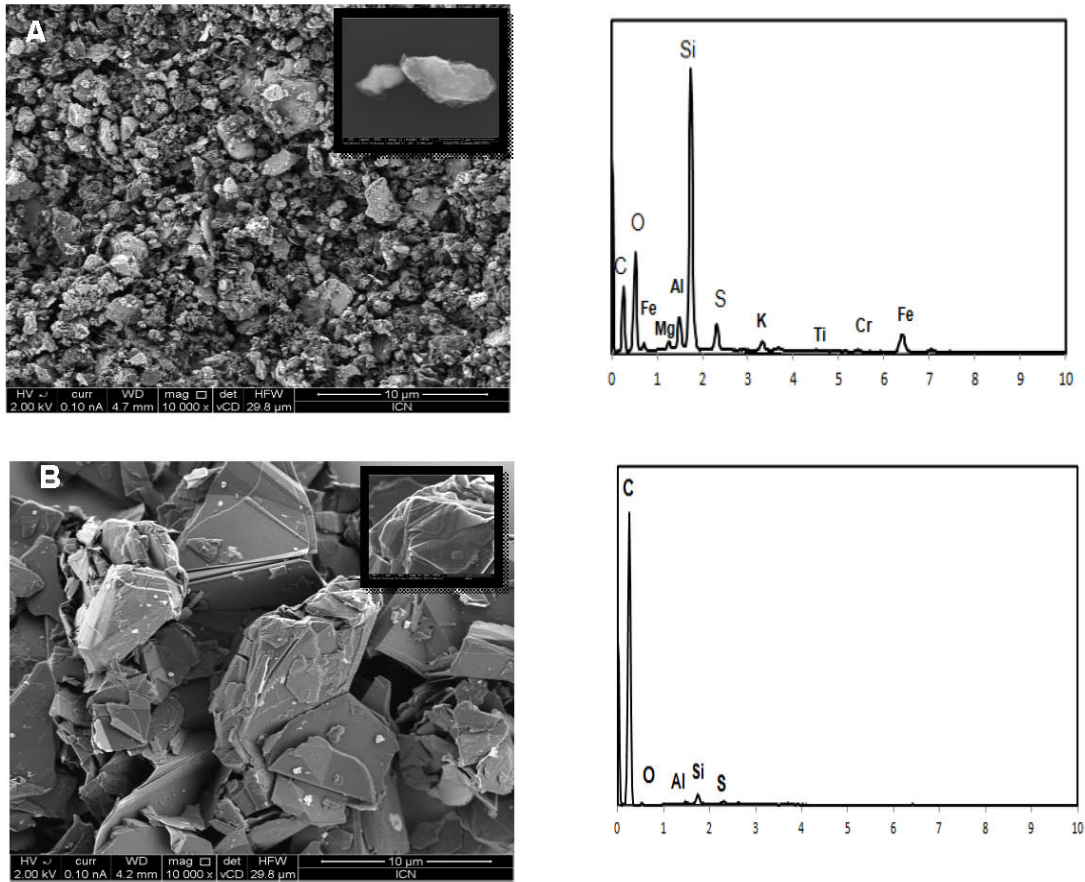


Figure 1. SEM images and EDS spectrum: a) Sungite and b) commercial carbon.

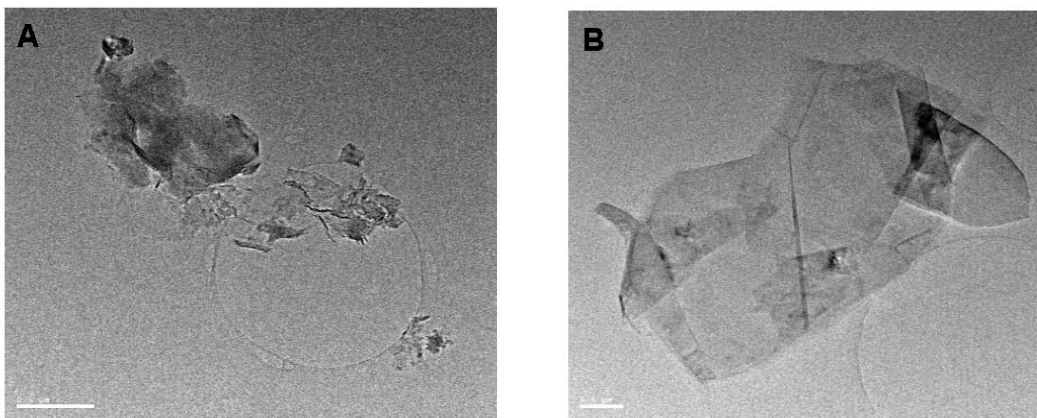


Figure 2. TEM images of a) sungite and b) commercial carbon.

The microstructure was investigated by TEM. The TEM micrographs at low magnification (Fig. 2) show, in both samples, agglomerated regions. As can be seen, the sungite samples are characterized by particles of smaller size than commercial carbon material, a fact that is in good agreement with SEM results.

## Electrochemical characterization

The kinetics of lithium intercalation in any composite electrode materials can be studied using cyclic voltammograms (CV). Figure 3 shows the CV peaks corresponding to insertion and desinteration of Lithium.

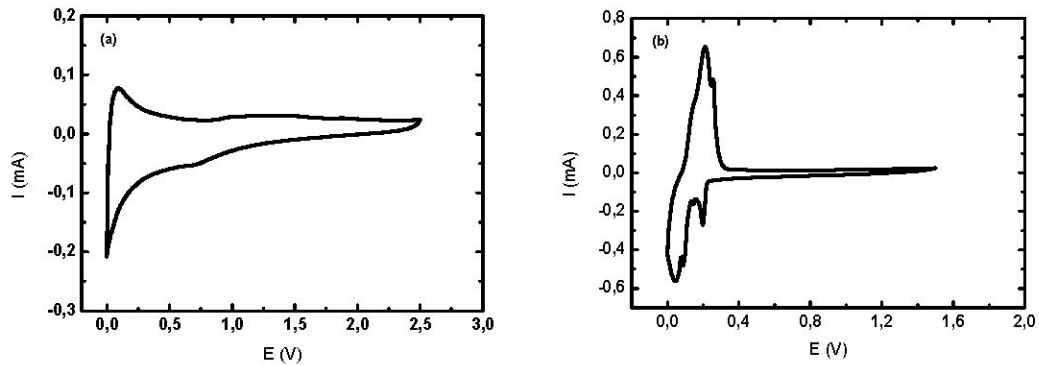


Figure 3. Cyclic voltammograms at  $0.1\text{mVs}^{-1}$ : a) Sungite electrode and b) commercial carbon electrode.

Figure 4 (a) displays the discharge capacities versus the cycle number. During the first cycle, the discharge capacities of commercial carbon and sungite samples were about  $200$  and  $110\text{mAh g}^{-1}$  respectively. Initially, the commercial carbon samples exhibited higher discharge capacity, than sungite electrodes. The discharge capacity of the commercial carbon electrodes increase with cycling and after the 4th cycle remains around a constant value of  $250\text{mA h g}^{-1}$ . After the 4th cycle, the sungite electrodes present, whit increasing cycle number, a small decrease in the discharge capacity values. The charge-discharge profiles of studied electrodes are illustrated in Figure 4 (b-c). They were obtained at  $0.5\text{C}$  rate, at cut-off potentials ranges of  $2.50 - 0.00\text{V}$  and  $1.5 - 0.0\text{V}$ , for sungite and commercial carbon respectively. A magnification, in the  $0.0 - 0.4\text{V}$  potential range, was made to better observe the plateau. All observed plateau potentials in the charge-discharge profiles are in a good agreement with CV peaks shown in Fig. 3.

The discharge capacities, after 14<sup>th</sup> cycles, were  $146\text{mAh g}^{-1}$  and  $258\text{mAh g}^{-1}$  for sungite and commercial carbon electrode respectively. The specific discharge capacity of commercial carbon was higher than that for sungite carbon electrodes.

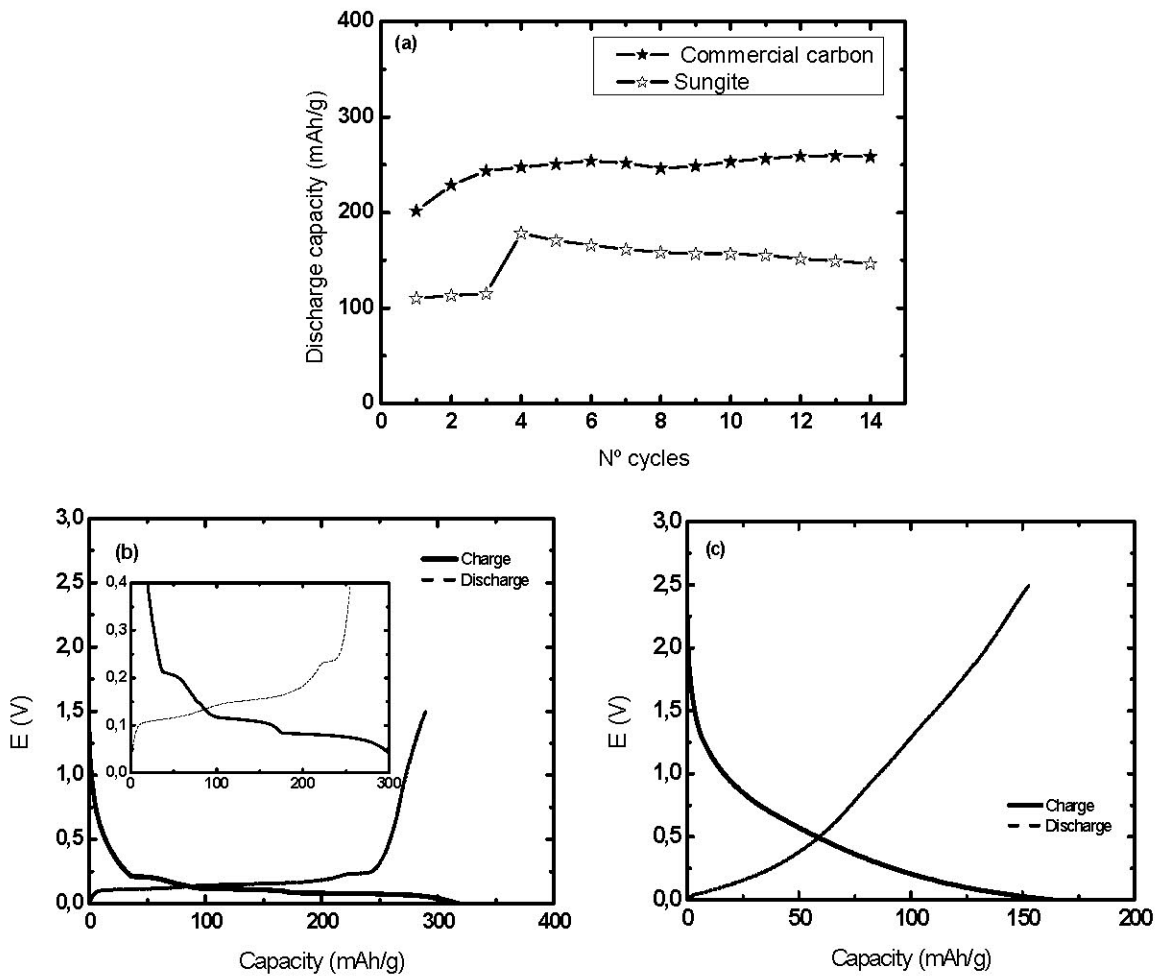


Figure 4. a). Discharge capacity vs. cycles number. Charge - discharge profiles of b). Commercial carbon electrode and c). Sungite electrode.

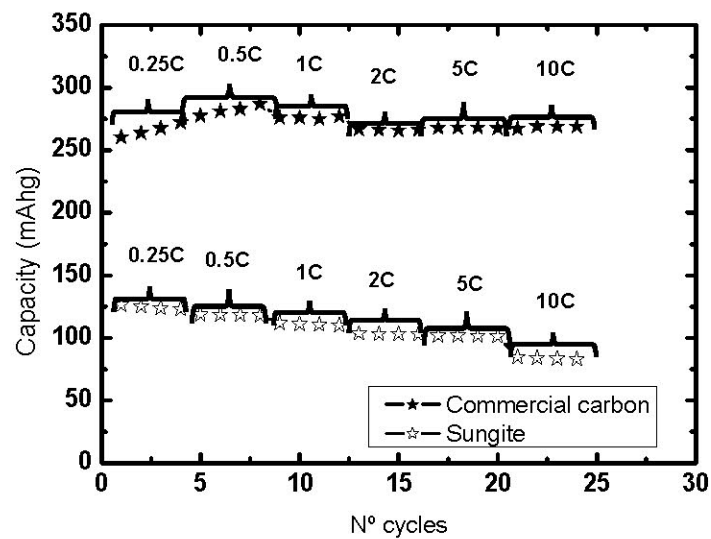


Figure 5. Discharge capacity vs. N° cycle, at different current discharge.

Figure 5 shows different discharge capacity vs.  $N^{\circ}$  cycles plots, at different discharge rates. The sungite electrodes show a decrease of discharge capacity values, when discharge current (I) increases. However, the commercial carbon electrodes exhibited that the capacity is slightly affected by the increase in current. Consequently, taking into consideration the rate capability results, it is apparent that commercial carbon electrodes present better electrochemical performance.

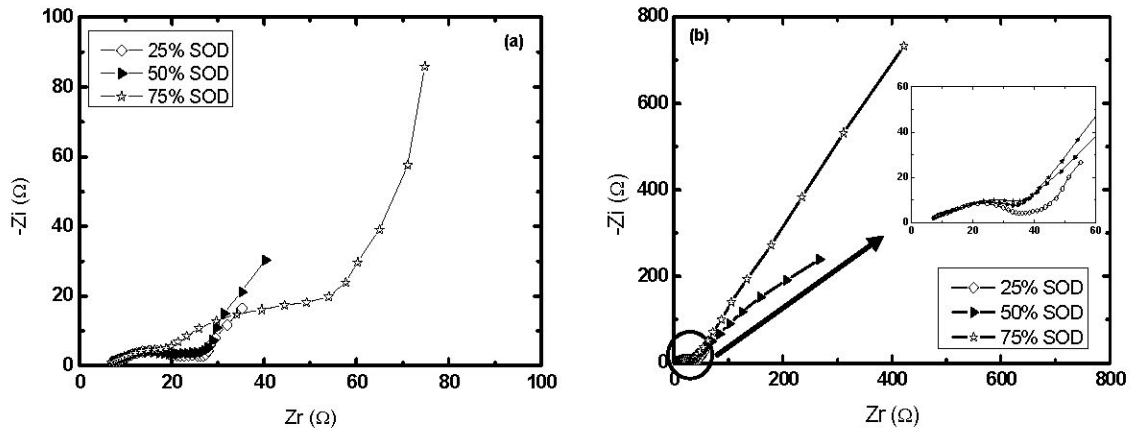


Figure 6. Nyquist's diagrams for a). Commercial carbon electrode b). Sungite electrode.

Nyquist diagrams corresponding to the studied samples are presented in Figures 6. The diagrams show, at the high frequency region, a phase angle close to  $45^{\circ}$  that is characteristic of a porous structure. The high frequency semicircle is due to the formation of the SEI (solid-electrolyte interphase) film. The capacitive loop, at the intermediate range of frequencies, is associated with the parallel connection of the electrical double layer ( $C_{dl}$ ), the charge transfer resistance ( $R_t$ ) related to the intercalation/deintercalation of lithium ions. For lower frequencies a diffusional impedance type is shown. For both electrode, impedance values increases with increasing state of discharge (% SOD). The sungite electrode exhibited higher impedance values. It is apparent that resistance values for the high frequency loop are lower for Sungite samples that could be related to the presence of a SEI with poor passivating properties.

## Conclusions

In this paper is presented the methodology used to prepare and characterize the reversible and irreversible capacity and cyclic stability of graphite materials as anodes in lithium-ion batteries of commercial carbon (CR 1296) and sungite material. Preliminary results allow us to understand the storing of lithium in sungite. In sungite lithium does not form stable compounds as seen by the absence of plateau and peaks in the voltammogram. The low carbon content in sungite is produced less SEI, lower resistant are due for the lower SEI.



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